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**D-80538 München (DE)**(54) **Process for production of polyurethane foam.**

(57) A process for producing a polyurethane foam, which comprises reacting a polyol component containing a benzylic ether type phenolic resin having hydroxymethyl groups with an organic polyisocyanate component in the presence of an organotin type urethanization catalyst, a tertiary amine type blowing catalyst and water.

Said process is free from the problems of the prior art; uses no fluorine-containing halogenated hydrocarbon as a blowing agent; and yet enables in-situ production of polyurethane foam by the use of a spray foaming machine in any season of the year.

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## Background of the Invention

## (1) Field of the Invention

5 The present invention relates to a process for producing a polyurethane foam. More particularly, the present invention relates to a process for producing a polyurethane foam, which uses no blowing agent such as fluorine-containing halogenated hydrocarbon or the like and yet enables in-situ production of polyurethane foam by the use of, for example, a spray foaming machine.

## 10 (2) Prior Art

Rigid polyurethanes have been applied to buildings by in-situ spray foaming, for the purposes of the moisture condensation prevention, heat insulation, etc. of said buildings. The foaming solutions heretofore used for production of polyurethane foam contain a fluorine-containing halogenated hydrocarbon as a  
15 blowing agent in an amount of about 15-40% by weight based on the foaming solution. The use of the fluorine-containing halogenated hydrocarbon, however, is said to be totally banned in near future in connection with the problem of ozone layer destruction.

Water, etc. are being investigated as a substitute for the fluorine-containing halogenated hydrocarbon. In using such a substitute blowing agent to achieve the same free rise density (e.g. 20 kg/m<sup>3</sup>) as obtained  
20 with conventional blowing agents, about 40% of an isocyanate component used together with a polyol component is consumed for the formation of urea bond, inviting reduction in physical properties of foam obtained, such as reduction in adhesivity and occurrence of fragility.

Further, in using water as a blowing agent, there arises two-step foaming owing to the difference between (1) the reaction rate between isocyanate component and polyol component and (2) the reaction  
25 rate between isocyanate component and water, which tends to generate a gap between the foam produced and the surface of the material to which the foam is adhered; in the winter when the reaction between isocyanate component and water is inactive, it is natural that no desired foam of low density is difficult to obtain; moreover, there arise problems which make difficult the control of spray foaming, such as increase  
30 in component ratio (ratio of NCO component and OH component), increase in foaming solution viscosity and the like.

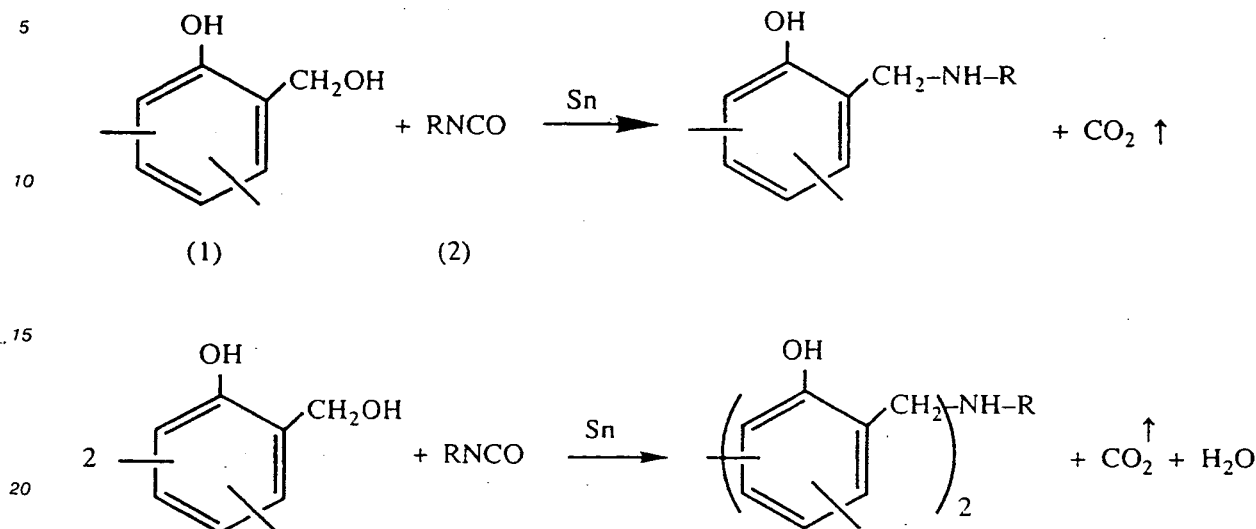
## Object and Summary of the Invention

The object of the present invention is to provide a process for producing a polyurethane foam, which is  
35 free from the above-mentioned problems of the prior art and which uses no fluorine-containing halogenated hydrocarbon as a blowing agent and yet enables in-situ production of polyurethane foam by the use of a spray foaming machine in any season of the year.

The present inventors paid attention to a fact that, as shown in the following reaction formula A, a phenol (1) having a hydroxymethyl group at the o-position, when reacted with an organic isocyanate (2) in  
40 the presence of an organotin type urethanization catalyst, generates carbon dioxide [e.g. Hybrid Phenolic/Urethane Foams, Anthony J. PaPa and Frank E. Critchfield, Journal of Cellular Plastics, 258, September/October (1979)]. Also, the present inventors tried to use a phenolic resin having hydroxymethyl groups at the o-position as a polyol component for formation of polyurethane foam and utilize the resulting carbon  
45 dioxide as a blowing agent for formation of foam.

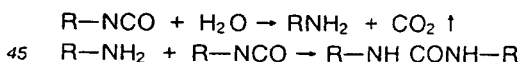
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Reaction formula A

25 However, a novolac type phenolic resin (which is a phenolic resin having hydroxymethyl groups at the o-position) is generally solid and insoluble in solvents, and is therefore unusable as a polyol component. A resole type phenolic resin generally contains at least 20% of water; when the resin is used as a polyol for reaction with an isocyanate, a large proportion of said water reacts with the isocyanate, making it difficult to control the reaction. Reduction in water content of the resin invites an increase in the viscosity of the resin, incurring reduction in stirring efficiency, etc. Hence, the present inventors found that a benzylic ether type phenolic resin having, for example, a water content of 0.5% or less and a viscosity of 1,000-20,000 cp can be used as a polyol component in the production of polyurethane foam.

30 However, a study indicated that foaming is insufficient only with the carbon dioxide generated from the reaction between the hydroxymethyl groups of benzylic ether type phenolic resin and organic isocyanate and no desired foam of low density (high expansion ratio) can be obtained. Hence, the present inventors made further study and found out that by adding water as a foaming aid and further adding a tertiary amine type urethanization catalyst for the promotion of the reaction between water and isocyanate, it is possible to effectively utilize not only the above-mentioned reaction of formula A but also the urea bond formation reaction represented by the following reaction formula B (this reaction generates carbon dioxide as well) to produce an intended polyurethane foam of low density. The finding has led to the completion of the present invention.

Reaction formula B

50 The present invention provides a process for producing a polyurethane foam, which comprises reacting a polyol component containing a benzylic ether type phenolic resin having hydroxymethyl groups with an organic polyisocyanate component in the presence of an organotin type urethanization catalyst, a tertiary amine type blowing catalyst and water.

Detailed Description of the Invention

The present invention is hereinafter described in detail.

55 The process for production of polyurethane foam according to the present invention is characterized by using, as at least part of the essential polyol component, a benzylic ether type phenolic resin having hydroxymethyl groups. Herein, the "benzylic ether type phenolic resin having hydroxymethyl groups" is a phenolic resin obtained by reacting phenol and aldehyde in the presence of a catalyst comprising, for

example, a naphthenate or carboxylate of a bivalent metal, at 100-130 °C; is a viscous liquid, a semisolid or a solid depending upon the polymerization conditions; and can be produced, for example, by the process described in Japanese Patent Publication No. 50873/1972.

The benzylic ether type phenolic resin having hydroxymethyl groups (hereinafter referred to simply as benzylic ether type phenolic resin, in some cases) can have a hydroxyl value of 300-700 mgKOH/g, preferably 450-600 mgKOH/g.

In the present invention, the benzylic ether type phenolic resin may be used as a single polyol component, but is preferably used in combination with other polyol because its use as a single polyol component gives a too rapid curing rate and the resulting foam has cracks, etc. inside. The other polyol usable is polyols conventionally used in production of polyurethane and includes, for example, dihydric alcohols such as ethylene glycol, diethylene glycol, neopentyl glycol, 1,4-butanediol, 1,6-hexanediol, 1,4-cyclohexanedimethanol and the like; trihydric or higher alcohols such as glycerine, trimethylolpropane, tris-(2-hydroxyethyl) isocyanurate, pentaerythritol and the like; and polyester polyols, polyether polyols, ethylenediamine type polyols, ether type Mannich polyols, etc. all obtained from said polyhydric alcohols.

The above other polyols can be used singly or in combination of two or more. Of them, ethylenediamine type polyols and ether type Mannich polyols are particularly preferable.

When the other polyol is used in combination with the benzylic ether type phenolic resin, the amount of the benzylic ether type phenolic resin used is not particularly restricted and can vary in a wide range depending upon the desired properties of foam obtained, the kind of the other polyol used in combination, etc. The amount, however, is generally 20-100% by weight, preferably 30-80% by weight based on the total amount of the polyols used.

Meanwhile, the organic polyisocyanate component to be reacted with the polyol component include polyisocyanate compounds of aliphatic type, alicyclic type, aromatic type, aralkyl type, etc. having at least two isocyanate groups (-NCO) in the molecule, conventionally used in production of polyurethane, and can be exemplified by aromatic polyisocyanates such as 2,4-tolylene diisocyanate, 2,6-tolylene diisocyanate, a mixture of 2,4-tolylene diisocyanate and 2,6-tolylene diisocyanate, crude tolylene diisocyanate, methylene diphenyl diisocyanate (MDI), 4,4',4''-triphenyl methylene triisocyanate, polymethylene polyphenyl isocyanate (crude MDI) and the like, and aliphatic polyisocyanates such as hexamethylene-1,6-diisocyanate, hydrogenated MDI and the like. Of these, crude MDI is particularly preferable.

The proportion of the organic polyisocyanate component to the polyol component is preferably 1.0-1.5 in terms of (NCO equivalents)/(OH equivalents).

In the present invention, an organotin type urethanization catalyst is used in order to promote the reaction between the hydroxymethyl groups of the benzylic ether type phenolic resin and the isocyanate groups of the organic polyisocyanate component. The organotin type urethanization catalyst can be any organotin generally used in urethanization reaction and includes, for example, dibutyltin dilaurate, dibutyltin diacetate, dibutyltin dialkylmaleates, tin stearate and tin octylate. The amount of the organotin type urethanization catalyst used is not particularly restricted but is generally 0.1-14% by weight, preferably 0.4-9% by weight based on the benzylic ether type phenolic resin.

Also in the present invention, a tertiary amine type blowing catalyst is used in order to promote the reaction between water and isocyanate. The "blowing catalyst" refers to a catalyst having a reaction rate constant ratio  $[(K_2/K_1) \times 10^{-1}]$  of 10 or more wherein  $K_1$  and  $K_2$  (L/mole x hr) are, respectively, a reaction rate constant between tolylene diisocyanate (TDI) and diethylene glycol and a reaction rate constant between TDI and water [e.g. Journal of Cellular Plastics, 23, 461(1987)], both in the presence of said catalyst, and includes, for example, bis-2-dimethylaminoethyl ether, N,N',N''-trimethylamine, ethylethanolamine and pentamethyldiethylenetriamine.

The amount of the tertiary amine type blowing catalyst used is appropriately 2-10% by weight based on the organic polyisocyanate. Use of, as the main catalyst, a catalyst having a reaction rate constant ratio  $[(K_2/K_1) \times 10^{-1}]$  smaller than 10 gives rise to inconveniences such as increased foam density, lower reactivity in water, two-step foaming and the like, in some cases.

In the present invention, it is also possible to use as necessary, for the control of the reaction rate, other urethanization catalyst, in combination with the blowing catalyst, in an amount of 50% by weight or less, preferably 40% by weight or less based on the blowing catalyst. The other urethanization catalyst usable in combination includes, for example, tertiary amine type catalysts and derivatives thereof such as triethylenediamine, 2-methyltriethylenediamine, N,N-dimethylaminoethylmorpholine, 1-isobutyl-2-methylimidazole, 1,8-diazabicyclo[5,4,0]undecene-7, 1,5-diazabicyclo[4, 3, 0]nonene-5 and the like; and organic acid metal salt type catalysts such as cobalt naphthenate, tetra(2-ethylhexyl) titanate, ferric 2-ethylhexoate, cobalt 2-ethylhexoate, zinc naphthenate and the like.

In the present invention, water is used as a blowing aid. Since use of too large an amount of water tends to produce a foam of fragility, low adhesivity, etc., water is used in an amount of preferably 4% by weight or less, particularly preferably 2% by weight or less based on the organic polyisocyanate.

In the present invention, it is possible to add as necessary, for higher flame retardancy of foam obtained, a trimerization catalyst to form an isocyanurate. The trimerization catalyst usable includes, for example, tertiary amine type catalysts such as N,N',N''-tris(dimethylaminopropyl)hexahydro-S-triazine, 2,4,6-trisdimethylaminomethylphenol and the like; and organic acid metal salt type catalysts such as potassium acetate, potassium octanoate, potassium 2-ethylhexoate, sodium carbonate, iron oxalate and the like.

In the present invention, it is possible to as necessary add other additives which may be used in production of polyurethane foam. Such other additives include, for example, foam stabilizers such as adduct between dimethyl silicon and ethylene oxide or propylene oxide, cationic surfactant, anionic surfactant, nonionic surfactant and the like; flame retardants such as tris(2,3-dibromopropyl) phosphate, tris(2-chloroethyl) phosphate, trimethyl phosphate, triethyl phosphate, tributyl phosphate and the like; viscosity-reducing agents such as dibutyl phosphate, dioctyl phosphate, polypropylene carbonate and the like; fillers such as antimony trioxide, zeolite, percyllite and the like; and coloring agents such as pigment, dye and the like.

The production of a polyurethane foam using the above-mentioned various components can be conducted, for example, by mixing all components other than an organic polyisocyanate component to prepare a polyol composition, adding the organic polyisocyanate component to the composition and mixing them, pouring the resulting mixture into a die or spraying the mixture on the surface of a substrate by the use of, for example, a spray foaming machine, and then allowing foaming and curing to take place. The time required for foaming and curing is generally about 5-30 seconds.

The present invention is described more specifically below by way of Examples.

#### Example 1

In a 750-ml container were weighed the following components:

10 g of a benzylic ether type phenolic resin having hydroxymethyl groups (hydroxyl value = 596 mgKOH/g),

27.25 g of an ethylene diamine type polyol (hydroxyl value = 315 mgKOH/g) (XR FD-5080, a product of Asahi Glass Co., Ltd.),

0.25 g of an organotin type urethanization catalyst (dibutyltin alkylmaleate) (T-52NJ, a product of Katsuta Kako K.K.),

2.75 g of a tertiary amine type blowing catalyst (bis-2-dimethylaminoethyl ether) (DABCO BL-19, a product of Sankyo Air Products K.K.),

0.75 g of a foam stabilizer (a silicon type),

8 g of a flame retardant (triethyl phosphate) (TEP, a product of Daihachi Kagaku K.K.), and

1 g of water.

The above components were subjected to preliminary stirring. Thereto was added 50 g of crude polymethylene polyphenyl isocyanate (crude MDI) (Millionate MR-200, a product of Nippon polyurethane Industry Co., Ltd.). The resulting mixture was violently stirred at room temperature for 1-2 seconds, at 2,000 rpm by the use of a cage type stirrer to allow foaming and curing to take place in a cup-free state.

The cream time and rise time, density (free rise density) of the foam obtained are shown in Table 1.

Using the above components, foam was obtained by the use of a Gasmer spray blowing machine. The spray foaming property, foam condition, adhesion strength and ratio of isolated cells are shown in Table 1.

#### Examples 2 to 18

The procedure of Example 1 was repeated using the components and amounts shown in Table 1, to produce polyurethane foams. The cream time and rise time in a cup-free state, density (free rise density), spray foaming property, foam condition, adhesion strength and ratio of isolated cells are shown in Table 1.

Incidentally, the spray foaming property, foam condition, adhesion strength and ratio of isolated cells in Table 1 were evaluated according to following yardsticks.

Spray foaming property

The applicability of spray foaming was evaluated according to the following three-stage yardsticks.

- 5    ☒ : Applicability is good (there is neither two-stage foaming nor sagging, and foaming is completed in a good condition)
- ☐ : Applicability is possible (two-stage foaming and sagging are seen slightly but there is no appearance problem)
- ☐ : Applicability is poor (there are two-stage foaming, and application is impossible)

10    Foam condition

Foam condition was evaluated according to the following three-stage yardsticks.

- ☒ : Foam condition is good (there is neither shrinkage nor cracking)
- ☐ : Foam condition has slight defect (shrinkage, etc. are seen slightly)
- 15    ☐ : Foam condition is poor (there are shrinkage and cracking)

Adhesion strength

20    Spray foaming was conducted on a gypsum board, and the adhesion strength to the board was measured by a tensile test (JIS A 9256) and evaluated according to the following three-stage yardsticks.

- ☒ : Adhesion strength is good (adhesion strength is 2 Kgf/cm<sup>2</sup> or more)
- ☐ : Adhesion strength has slight problem (peeling, etc. are seen slightly and adhesion strength is 1 to less than 2 Kgf/cm<sup>2</sup>)
- 25    ☐ : Adhesion strength is bad (adhesion strength is less than 1 Kgf/cm<sup>2</sup>)

Ratio of isolated cells

30    The condition of foams of foamed material was examined in terms of ratio of isolated cells and evaluated according to the following three-stage yardsticks. When the ratio of isolated cells is smaller, the foam material has a higher thermal conductivity and a lower heat-insulating effect.

- ☒ : Cells are nearly isolated (ratio of isolated cells is 70% or more)
- ☐ : Ratio of isolated cells is small (ratio of isolated cells is 40% to less than 70%)
- ☐ : Ratio of continuous cells is large (ratio of isolated cells is less than 40%)

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Table1-1

Examples									
	1	2	3	4	5	6	7	8	9
Components									
Crude MDI	50	50	50	50	50	50	50	50	50
Benzylic ether type phenolic resin	10	26	20	10	10	10	10	10	35.1
Polyols									
FD-5080	27.25	11.25	17.25	19	15	19	19	8.9	-
SO-200	-	-	-	7.5	-	8.2	7.5	17.35	-
Ar-3775	-	-	-	-	10.25	-	-	-	-
Organotin type urethanization catalyst	0.25	0.25	0.25	0.25	0.25	0.25	0.25	0.25	0.25
Blowing catalyst	2.75	2.75	2.75	2.00	2.75	2.00	2.00	2.75	2.75
Other urethanization catalysts									
Polycat 77	-	-	-	0.75	-	0.4	-	-	-
DABCO 33LV	-	-	-	-	-	0.4	0.75	-	-
Trimerization catalyst (NKC)	-	-	-	0.75	-	-	0.75	-	-
Foam stabilizer	0.75	0.75	0.75	0.75	0.75	0.75	0.75	0.75	0.75
Flame retardant	8	8	8	8	10	8	8	8	11
Water	1	1	1	1	1	1	1	2	0.15
Cream time (sec)	2	2	2	2	1.5	1.5	1.5	2	3.5
Rise time (sec)	10	15	10	12	9	10	9	12	13
Density (kg/m <sup>3</sup> )	25.0	12.0	23.0	24.5	25.0	25.0	21.0	15.0	15.6
Foaming property	○	○	○	○	○	○	○	○	○
Foam condition	○	○	○	○	○	○	○	○	○
Adhesion Strength	○	○	○	○	○	○	○	○	○
Ratio of isolated cells	○	○	○	○	○	○	○	○	○

Table 1-2

Examples									
	10	11	12	13	14	15	16	17	18
Components									
Crude MDI	50	50	50	50	50	50	50	50	50
Benzylic ether type phenolic resin	10	10	10	10	10	10	10	10	10
Polyols									
FD-5080	28.5	29.0	27.25	27.35	15	27.25	27.25	19.0	29.0
SO-200	-	-	-	-	-	-	-	7.5	-
Ar-3775	-	-	-	-	10	-	-	-	-
Organotin type urethanization catalyst	0.25	0.25	0.1	1.4	0.25	0.25	*0.25	*0.25	*0.25
Blowing catalyst	1.50	1.00	2.75	2.75	5.0	*2.75	2.75	*2.00	*1.00
Other urethanization catalysts									
Polycat 77	-	-	-	-	-	-	-	0.75	-
DABCO 33 LV	-	-	-	-	-	-	-	-	-
Trimerization catalyst (NKC)	-	-	-	-	-	-	-	0.75	-
Foam stabilizer	0.75	0.75	0.75	0.75	0.75	0.75	0.75	0.75	0.75
Flame retardant	8	8	8.15	6.75	8	8	8	8	8
Water	1	1	1	1	1	1	1	1	1
Cream time (sec)	3.5	4	2	2	1	2	2	2	4
Rise time (sec)	12	13	12	9	10	9	8	10	12
Density (kg/m <sup>3</sup> )	35.0	28.8	31.0	32.5	23.7	25.8	26.4	25.5	30.2
Foaming property	○	○	○	○	○	○	○	○	○
Foam condition	○	○	○	○	○	○	○	○	○
Adhesion Strength	○	○	○	○	○	○	○	○	○
Ratio of isolated cells	○	○	○	○	○	○	○	○	○

FD-5080 = ethylenediamine type polyol, SO-200 = sorbitol type polyol

Ar-3775 = Mannich type polyol

Polycat 77 = N-methyl-N'-bis(3-dimethylaminopropylamine)

DABCO 33LV = diethyleneglycol solution containing 33% of triethyl diamine

NKC = glycerine solution containing 33% of potassium octylate

\* in Organotin type urethanization catalyst induces dibutyltin dialkylmaleate is used (in other Examples, dibutyltin dialkylaurate is used)

\* in Blowing catalyst induces bis-2-dimethylaminoethyl ether is used (in other Examples, pentamethylethylenetriamin is used)

#### Comparative Examples 1 to 6

The procedure of Example 1 was repeated using the components and amounts shown in Table 2, to produce a polyurethane foam. The cream time and rise time in a cup-free state, density (free rise density), spray foaming property, foam condition, adhesion strength and ratio of isolated cells are shown in Table 2.



The spray foaming property, foam condition, adhesion strength and ratio of isolated cells in Table 2 were evaluated according to following yardsticks.

Table2

Comparative Examples						
	1	2	3	4	5	6
Components						
Crude MDI	50	50	50	50	50	50
Benzylic ether type phenolic resin	-	4	10	10	10	10
Polyols						
FD-5080	30.12	26.32	30	27.5	29.25	29
SO-200	-	7.53	-	-	-	-
Ar-3775	7.53	-	-	-	-	-
Organotin type urethanization catalyst	0.50	0.50	0.25	2.75	-	0.25
Blowing catalyst	2.68	2.68	-	-	-	0.5
Other urethanization catalysts						
Polycat 77	-	-	-	-	-	-
DABCO 33 LV	-	-	-	-	-	-
Trimerization catalyst (NKC)	1.08	1.08	-	-	1	0.5
Foam stabilizer	0.75	0.75	0.75	0.75	0.75	0.75
Flame retardant	5.66	5.66	8.00	8.00	8.00	8.00
Water	1.68	1.48	1	1	1	1
Cream time (sec)	7	6	7	5	5	5
Rise time (sec)	36	28	19	12	15	14
Density (kg/m <sup>3</sup> )	25.0	25.2	31.6	32.5	33.3	28.3
Foaming property	×	×	×	○	○	○
Foam condition	○	○	○	×	×	○
Adhesion Strength	×	×	○	○	○	○
Ratio of isolated cells	⊙	⊙	×	×	×	×

Organotin type urethanization catalyst = dibutyltin dialkylmaleate  
Blowing catalyst = bis-2-dimethylaminoethyl ether

As is appreciated from Table 1, the foams according to the present invention are superior to the foams according to Comparative Examples, in properties, particularly in adhesion strength.

According to the process of the present invention, by appropriately using a benzylic ether type phenolic resin, an organotin type urethanization catalyst, a tertiary amine type blowing catalyst, water, etc., the resulting foam can have a desired expansion ratio, for example, a high free rise density of 40 kg/m<sup>3</sup> or less, particularly 30 kg/m<sup>3</sup> or less.

In the polyurethane foam produced by the present process, the low adhesivity, fragility, etc. (these have been the problems of conventional foams obtained by water foaming) can be alleviated. Further in the present process, by only adding about 10% of a flame retardant as a viscosity-reducing agent, a foaming solution of 100-500 cp can be prepared easily and a foam of high expansion ratio can be produced. Meanwhile, when it is desired to achieve a high expansion ratio by spray foaming based on conventional water foaming, with the component ratio (ratio of NCO component and OH component) fixed at 1:1, it is necessary to make high the proportion of water in OH component (a large amount of water must be added); as a result, other OH component need be a polyol of high hydroxyl value, i.e. a polyol of high molecular weight; in order to reduce the resulting high viscosity, a viscosity-reducing agent (e.g. flame retardant) must be added in a large amount. As a result, there arises reduction in strength and adhesivity of foam obtained.

### Claims

1. A process for producing a polyurethane foam, which comprises reacting a polyol component containing a benzylic ether type phenolic resin having hydroxymethyl groups with an organic polyisocyanate component in the presence of an organotin type urethanization catalyst, a tertiary amine type blowing catalyst and water.
2. A process according to Claim 1, wherein the benzylic ether type phenolic resin having hydroxymethyl groups, contained in the polyol component has a hydroxyl value of 300-700 mgKOH/g.
3. A process according to Claim 1, wherein the proportion of the benzylic ether type phenolic resin having hydroxymethyl groups, contained in the polyol component is 20-100% by weight based on the polyol component.
4. A process according to Claim 1, wherein the proportion of the organic polyisocyanate component to the polyol component is 1.0-1.5 in terms of NCO equivalents/OH equivalents.
5. A process according to Claim 1, wherein the proportion of the organotin type urethanization catalyst is 0.1-14% by weight based on the benzylic ether type phenolic resin.
6. A process according to Claim 1, wherein the tertiary amine type blowing catalyst has a reaction rate constant ratio  $[(K_2/K_1) \times 10^{-1}]$  of at least 10.0 wherein  $K_1$  and  $K_2$  are, respectively, a reaction rate constant between tolylene diisocyanate and diethylene glycol and a reaction rate constant between tolylene diisocyanate and water, both in the presence of said tertiary amine type blowing catalyst.
7. A process according to Claim 6, wherein the tertiary amine type blowing catalyst contains other urethanization catalyst.
8. A process according to Claim 1, wherein the proportion of the tertiary amine type blowing catalyst is 2-10% by weight based on the organic polyisocyanate.
9. A process according to Claim 1, wherein the proportion of water is 4% by weight or less based on the organic polyisocyanate.



European Patent  
Office

## EUROPEAN SEARCH REPORT

Application Number  
EP 94 11 7024

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION
X	GB-A-1 268 440 (MIDWEST RESEARCH) * claims 1-4,9,13 * * page 1, line 35 - line 46 * * page 2, line 9 - line 30 * * page 3, line 32 - line 49 * ---	1	C08G18/54 C08G18/16 /(C08G18/54, 101:00)
A	FR-A-2 046 987 (BAYER) * claims 1,6 * * page 6, line 13 - line 38 * * page 13, line 15 - page 14, line 8 * ---	1	
A	US-A-4 448 951 (J.P. RUPERT ET AL.) * claims 1,2 * * column 5, line 57 - line 65 * * column 6, line 43 - line 46 * ---	1	
A	US-A-4 454 253 (J.R. MURPHY ET AL.) * claims 1,3,5 * * column 4, line 48 - line 53 * * column 5, line 3 - line 46 * -----	1	
			TECHNICAL FIELDS SEARCHED (Int. CL. 6)
			C08G
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 10 January 1995	Examiner Van Puymbroeck, M
<b>CATEGORY OF CITED DOCUMENTS</b>			
X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document		T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons ----- & : member of the same patent family, corresponding document	